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Materials Science and Engineering A

iournal homepage: www.elsevier.com/locate/msea

Interfacial microstructure and mechanical properties of SnBi/Cu joints by alloying Cu substrate

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a r t i c l e i n f o

Article history: Received 26 July 2011 Received in revised form 18 October 2011 Accepted 19 October 2011 Available online 25 October 2011

Keywords: Sn–Bi solder $Cu₃Sn$ Void, Bi segregation Interfacial embrittlement Cu alloys

A B S T R A C T

It is well known that some discontinuous Bi particles and voids often appear at the interfaces for the SnBi/Cu couples, leading to the interfacial embrittlement during the thermo-aging procedure. In the current study, the experimental results confirmed that Bi segregation at the SnBi/Cu interface mainly originated from the Bi diffusion during reflowing and aging procedure. Small amounts of Ag, Al, Sn or Zn elements were deliberately added into the Cu substrate to restrain the interfacial Bi embrittlement of the SnBi/Cu couples. It does not only restrain the Bi segregation, but also eliminate the formation of voids at the interfaces. Besides, it is interesting to find that the addition of these elements above can significantly improve the mechanical properties of SnBi/Cu alloy joints even after long-term aging. Based on the experimental evidence, it is suggested that alloying Cu substrate is beneficial to the wide application of SnBi and other lead-free solders, and has the potential of being a common substrate in the electronic packaging field in the future.

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1. Introduction

It is well known that the intermetallic compound (IMC) layers always form at the interfaces when molten solders wet on the substrates [\[1–4\].](#page--1-0) With prolonging aging time, not only the thickness of IMC layer increases, but also the $Cu₃Sn$ layer forms on the Cu substrate. Most previous results have confirmed that the interfacial bonding strength often deteriorates with increasing the thickness of the IMC layer under high-temperature conditions [\[5–7\].](#page--1-0) However, for some solder joints, the increasing thickness of the IMC layer is not the exclusive reason for the decrease of the bonding strength. For example, the $Cu₃Sn$ layer often compromises the mechanical properties of solder joints due to the formation of voids at the interface. Besides, the Bi segregation at interfaces can also dramatically deteriorate the bonding strength [\[2–4\].](#page--1-0) For example, Liu et al. [\[3\]](#page--1-0) have reported that the Bi segregation at the $Cu/Cu₃Sn$ interface led to the sharp decrease in the mechanical properties of Cu/SnBi couples after aging at 120 \degree C for 7 days, which greatly restrained the wide usage of Sn–Bi solder in the electronic packaging field.

In order to restrict the Bi interfacial segregation, Liu et al. [\[4\]](#page--1-0) and Zhu et al. [\[8\]](#page--1-0) have tried to employ the electrodepositing Ag or Ni thin films onto the Cu substrate to prevent the interfacial

Bi embrittlement of SnBi/Cu joints. But there are still some arguments on the main source and the format of the Bi segregation at the SnBi/Cu interfaces [\[2–4,9\].](#page--1-0) Besides, some important scientific problems should be clarified: (1) how do the Bi atoms segregate into the SnBi/Cu interface; (2) how to understand the nature of the interfacial embrittlement in the SnBi/Cu joint after long aging time; (3) how to effectively prevent the interfacial Bi embrittlement of the SnBi/Cu joint for its potential industrial application?

To clarify these problems above, we design some special experiments to further reveal the source of Bi segregation and the interfacial Bi embrittlement in the SnBi/Cu couples. The primary experimental results have confirmed that the Bi segregation mainly originates from the Bi diffusion of the SnBi solder and the interfacial Bi embrittlement of the SnBi/Cu can be effectively eliminated by alloying Cu substrate [\[10\].](#page--1-0) Based on the new experimental results, we propose new strategy to restrain the formation of voids and the interfacial Bi embrittlement of the SnBi/Cu couples by alloying Cu substrate.

2. Experimental procedure and design

In this study, Cu, Cu–Xalloys (X= 2.5 or 18.7Ag, 2.3Al, 3Sn, 5 or 10 or 30Zn) were used as substrates and the eutectic Sn–58 wt%Bi was employed as solder. Cu, Cu–X alloys and SnBi solder were cut and ground with 800#, 1000#, 2000# SiC paper,then carefully polished by the polishing pastes, respectively. All the SnBi/Cu and SnBi/Cu-X alloy couples were kept in an oven with a constant temperature of

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^{0921-5093/\$} – see front matter © 2011 Elsevier B.V. All rights reserved. doi:[10.1016/j.msea.2011.10.078](dx.doi.org/10.1016/j.msea.2011.10.078)

200 ℃ for 6 min. One group of the as-reflowed samples was isothermally aged at 120 ◦C for different times to measure the mechanical properties. Tensile tests were performed with an INSTON 8871 testing machine at an average strain rate of about 5×10^{-5} s⁻¹ at room temperature in air. Another group of as-reflowed samples was isothermally aged at 200 \degree C for various durations so as to reveal the Bi segregation under the liquid-state aging condition. All the samples were observed by LEO supra 35 scanning electron microscope (SEM).

Concerning the formation of the Bi segregation at the $Cu/Cu₃Sn$ interface, Shang et al. [\[9\]](#page--1-0) and Liu et al. [\[2–4\]](#page--1-0) did not propose a clear model. To better understand the formation of the Bi segregation, three different samples were designed, denoted as A, B and C, respectively, as illustrated in Fig. 1. For sample A, the SnBi solder firstly reacted with the Cu substrate to form one Cu–Sn IMC layer at the interface. Then the excess SnBi solder was removed by grinding and polishing. The IMC layer and the SnBi solder (\sim 100 μm) remained on the Cu substrate. Next, pure Sn was put on the SnBi solder and reacted with the Cu substrate at 260° C for 90 min, as displayed in Fig. 1. Since Cu firstly reacted with SnBi solder, the pre-existed Bi atoms of the IMC layer precipitated as particles at the $Cu/Cu₃$ Sn interface with prolonging the aging time if the origin of Bi segregation came from these Bi atoms which have dissolved in the Cu–Sn IMC layer during the reflowing procedure. Besides, the diffusion path of Bi atoms may be another main source for the Bi segregation at the Cu/Cu₃Sn interface. Then we designed other two samples B and C, pure Sn solder firstly reacted with the Cu substrate at 260 °C for 10 min to form the Cu–Sn IMC layers at the interface, as displayed in Fig. 1. Afterwards, the excess Sn solder was removed by etching so that only the Cu–Sn IMC layers kept on the Cu substrate for the sample B. But the Sn layer (\sim 100 μ m) remained on the Cu substrate after grinding for the sample C. The Cu–Sn IMC layers of the samples B and C must not contain Bi atoms

because the Cu substrate should firstly react with pure Sn. Then, the SnBi solder was put on the samples B and C for further reacting at 200 ℃ for 90 min. Therefore, the Bi atoms cannot be detected at the interface if the origin of Bi segregation comes from these Bi atoms. In contrast, the Bi atoms are easy to be detected at the interface of the samples B and C.

In order to investigate the Bi segregation mechanism under solid-state condition, samples D and E were designed during the experimental procedure. For sample D, SnBi solder firstly reacted with the Cu substrate at 200 \degree C for 10 min to form the Cu–Sn IMC layers at the interface, as displayed in Fig. 1. Afterwards, the excess SnBi solder was removed by etching so that only the Cu–Sn IMC layers kept on the Cu substrate for the sample D. And then a Sn thin film was clamped on the IMC layer to form sample D, and was aged at 120 \degree C for 16 days. Since Cu firstly reacted with SnBi solder, the pre-existed Bi atoms of the IMC layer precipitated as particles at the $Cu/Cu₃$ Sn interface with prolonging the aging time if the origin of Bi segregation came from these Bi atoms which have dissolved in the Cu–Sn IMC layer during the reflowing procedure. However, for sample E, the SnBi solder and Cu were clamped to form a solid diffusion sample, which was aged at 120° C for 17 days. At last, the interfacial microstructures of these samples were observed by LEO supra 35 SEM.

3. Experimental results

The mechanical properties of the SnBi/Cu and SnBi/Cu–X alloy joints have been tested. The dependence of tensile strength on the aging time of the SnBi/Cu and SnBi/Cu–X joints is shown in [Fig.](#page--1-0) 2. The tensile strength of the as-reflowed SnBi/Cu joint is about 155 MPa, and has a slight decrease down to 117.4 MPa when the samples were aged at 120° C for 4 days. However, the tensile strength of the SnBi/Cu joints was dramatically decreased

Fig. 1. Schematic diagram of five samples for revealing the Bi segregation (Note: the IMC layer cannot be described in this figure).

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